

FORM PTO-1390 (Modified)
(REV 11-2000)

U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

ATTORNEY'S DOCKET NUMBER

TRANSMITTAL LETTER TO THE UNITED STATES
DESIGNATED/ELECTED OFFICE (DO/EO/US)
CONCERNING A FILING UNDER 35 U.S.C. 371

217838US0PCT

U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR

10/n 30173

INTERNATIONAL APPLICATION NO.
PCT/EP00/07026INTERNATIONAL FILING DATE
21 July 2000PRIORITY DATE CLAIMED
6 August 1999

TITLE OF INVENTION

PREPARATION OF ALPHA-OXIDIZED CARBONYL COMPOUNDS

APPLICANT(S) FOR DO/EO/US

PUETTER Hermann et al.

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☒ This is an express request to begin national examination procedures (35 U.S.C. 371(f)). The submission must include items (5), (6), (9) and (24) indicated below.
4. ☒ The US has been elected by the expiration of 19 months from the priority date (Article 31).
5. ☒ A copy of the International Application as filed (35 U.S.C. 371 (c) (2))
 - a. ☐ is attached hereto (required only if not communicated by the International Bureau).
 - b. ☒ has been communicated by the International Bureau.
 - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☒ An English language translation of the International Application as filed (35 U.S.C. 371(c)(2)).
 - a. ☒ is attached hereto.
 - b. ☐ has been previously submitted under 35 U.S.C. 154(d)(4).
7. ☒ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371 (c)(3))
 - a. ☐ are attached hereto (required only if not communicated by the International Bureau).
 - b. ☐ have been communicated by the International Bureau.
 - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
 - d. ☒ have not been made and will not be made.
8. ☐ An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
9. ☒ An oath or declaration of the inventor(s) (35 U.S.C. 371 (c)(4)).
10. ☐ An English language translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371 (c)(5)).
11. ☐ A copy of the International Preliminary Examination Report (PCT/IPEA/409).
12. ☒ A copy of the International Search Report (PCT/ISA/210).

Items 13 to 20 below concern document(s) or information included:

13. ☒ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
14. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
15. ☒ A **FIRST** preliminary amendment.
16. ☐ A **SECOND** or **SUBSEQUENT** preliminary amendment.
17. ☐ A substitute specification.
18. ☐ A change of power of attorney and/or address letter.
19. ☐ A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1.821 - 1.825.
20. ☐ A second copy of the published international application under 35 U.S.C. 154(d)(4).
21. ☐ A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4).
22. ☐ Certificate of Mailing by Express Mail
23. ☒ Other items or information:

PCT/IB/304/Notice of Priority/Form PTO-1449

U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR 10/030173	INTERNATIONAL APPLICATION NO. PCT/EP/00/07026	ATTORNEY'S DOCKET NUMBER 217838US0PCT
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24. The following fees are submitted:.

BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)) :

- | | | |
|-------------------------------------|---|------------------|
| <input type="checkbox"/> | Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO | \$1040.00 |
| <input checked="" type="checkbox"/> | International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO | \$890.00 |
| <input type="checkbox"/> | International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO | \$740.00 |
| <input type="checkbox"/> | International preliminary examination fee (37 CFR 1.482) paid to USPTO but all claims did not satisfy provisions of PCT Article 33(1)-(4) | \$710.00 |
| <input type="checkbox"/> | International preliminary examination fee (37 CFR 1.482) paid to USPTO and all claims satisfied provisions of PCT Article 33(1)-(4) | \$100.00 |

ENTER APPROPRIATE BASIC FEE AMOUNT =

Surcharge of **\$130.00** for furnishing the oath or declaration later than ☐ 20 ☐ 30 months from the earliest claimed priority date (37 CFR 1.492 (e)).

CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE	
Total claims	14 - 20 =	0	x \$18.00	\$0.00
Independent claims	1 - 3 =	0	x \$84.00	\$0.00
Multiple Dependent Claims (check if applicable).			<input type="checkbox"/>	\$0.00

Multiple Dependent Claims (check if applicable).

TOTAL OF ABOVE CALCULATIONS =

- ☐ Applicant claims small entity status. See 37 CFR 1.27). The fees indicated above are reduced by 1/2.

SUBTOTAL =

Processing fee of **\$130.00** for furnishing the English translation later than ☐ 20 ☐ 30 months from the earliest claimed priority date (37 CFR 1.492 (f)).

TOTAL NATIONAL FEE =

Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31) **(check if applicable)**.

TOTAL FEES ENCLOSED =

Amount to be: refunded
charged

- a. ☒ A check in the amount of \$890.00 to cover the above fees is enclosed.
- b. ☐ Please charge my Deposit Account No. _____ in the amount of _____ to cover the above fees.
A duplicate copy of this sheet is enclosed.
- c. ☒ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 15-0030 A duplicate copy of this sheet is enclosed.
- d. ☐ Fees are to be charged to a credit card. **WARNING:** Information on this form may become public. **Credit card information should not be included on this form.** Provide credit card information and authorization on PTO-2038.

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO:



22850

Surinder Sachar
Registration No. 34,423

SIGNATURE

Norman F. Oblon

NAME _____

24,618

REGISTRATION NUMBER

DATE _____

217838US-0PCT

IN THE UNITED STATES PATENT & TRADEMARK OFFICE

IN RE APPLICATION OF: :

HERMANN PUETTER ET AL. :

SERIAL NO: NEW U.S. PCT APPLN. : ATTN: APPLICATION BRANCH
(Based on PCT/EP00/07026)

FILED: HEREWITH :

FOR: PREPARATION OF ALPHA-OXIDIZED
CARBONYL COMPOUNDS

PRELIMINARY AMENDMENT

ASSISTANT COMMISSIONER FOR PATENTS
WASHINGTON, D.C. 20231

SIR:

Prior to examination on the merits, please amend the above-identified application as follows:

IN THE CLAIMS

Please amend the claims as shown in the marked-up copy following this amendment to read as follows:

5. (Amended) A process as claimed in claim 1, where the compound of the formula I is 2,2,3,3-tetramethoxypropanol, and the starting compound employed is methylglyoxal dimethyl acetal.

6. (Amended) A process as claimed in claim 1, where the anions of the metal salt (S) are derived from mineral acids.

7. (Amended) A process as claimed in claim 1, where the anions of the metal salt (S) are phosphate, sulfate, nitrate, perchlorate or halide.

8. (Amended) A process as claimed in claim 1, where the cations of the metal salt (S) are iron, nickel, platinum, palladium, cobalt, zinc, silver or copper.

9. (Amended) A process as claimed in claim 1, where the electrolysis liquid contains from 1 to 1000 ppm by weight of metal ions of the metal salt (S), based on the total amount of electrolysis liquid.

10. (Amended) A process as claimed in claim 1, where the electrolysis liquid contains a halogen-containing auxiliary electrolyte.

11. (Amended) A process as claimed in claim 1, where the electrolysis liquid essentially consists of

- a starting compound of the general formula V
- an alcohol of the general formula II
- a halogen-containing auxiliary electrolyte
- catalytic amounts of the metal salt (S)
- possibly the desired products of the general formulae I, III and IV
- possibly other by-products of electrolysis which are derived from the compounds of the general formulae I, II, III, IV and V, and
- if desired, other conventional co-solvents.

12. (Amended) A process as claimed in claim 1, where

- the proportion of the starting compounds and products of the general formulae I, III, IV and V and of the other by-products of electrolysis from the abovementioned compounds is from 1 to 70% by weight,

- the proportion of the alcohol of the general formula II is from 14.9 to 94.9% by weight,
 - the proportion of auxiliary electrolyte is from 0.1 to 5% by weight, and
 - the proportion of any co-solvents present is from 0 to 70% by weight,
- based on the electrolysis liquid.

13. (Amended) A process as claimed in claim 1, where the electrolysis is carried out in an undivided electrolysis cell.


14. (Amended) A process as claimed in claim 1, where the anodes employed are made of noble metals, noble-metal oxides, graphite or carbon materials, and the cathodes employed are made of iron, steel, nickel, zinc, noble metals, graphite or carbon materials.

REMARKS

Claims 1-14 are active in the present application. Claims 5-14 have been amended to remove multiple dependencies. No new matter is added. An action on the merits and allowance of claims is solicited.

Respectfully submitted,

OBLON, SPIVAK, McCLELLAND,
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217838US-0PCT

Marked-Up Copy
Serial No:
Amendment Filed on:
1-31-2002

IN THE CLAIMS

Please amend the claims as follows:

--5. (Amended) A process as claimed in [any one of claims 1 to 4] claim 1, where the compound of the formula I is 2,2,3,3-tetramethoxypropanol, and the starting compound employed is methylglyoxal dimethyl acetal.

6. (Amended) A process as claimed in [any one of claims 1 to 5] claim 1, where the anions of the metal salt (S) are derived from mineral acids.

7. (Amended) A process as claimed in [any one of claims 1 to 6] claim 1, where the anions of the metal salt (S) are phosphate, sulfate, nitrate, perchlorate or halide.

8. (Amended) A process as claimed in [any one of claims 1 to 7] claim 1, where the cations of the metal salt (S) are iron, nickel, platinum, palladium, cobalt, zinc, silver or copper.

9. (Amended) A process as claimed in [any one of claims 1 to 8] claim 1, where the electrolysis liquid contains from 1 to 1000 ppm by weight of metal ions of the metal salt (S), based on the total amount of electrolysis liquid.

10. (Amended) A process as claimed in [any one of claims 1 to 9] claim 1, where the electrolysis liquid contains a halogen-containing auxiliary electrolyte.

11. (Amended) A process as claimed in [any one of claims 1 to 10] claim 1, where the electrolysis liquid essentially consists of

- a starting compound of the general formula V

- an alcohol of the general formula II
- a halogen-containing auxiliary electrolyte
- catalytic amounts of the metal salt (S)
- possibly the desired products of the general formulae I, III and IV
- possibly other by-products of electrolysis which are derived from the compounds of

the general formulae I, II, III, IV and V, and

- if desired, other conventional co-solvents.

12. (Amended) A process as claimed in [any one of claims 1 to 11] claim 1, where

- the proportion of the starting compounds and products of the general formulae I, III, IV and V and of the other by-products of electrolysis from the abovementioned compounds is from 1 to 70% by weight,
- the proportion of the alcohol of the general formula II is from 14.9 to 94.9% by weight,
- the proportion of auxiliary electrolyte is from 0.1 to 5% by weight, and
- the proportion of any co-solvents present is from 0 to 70% by weight,

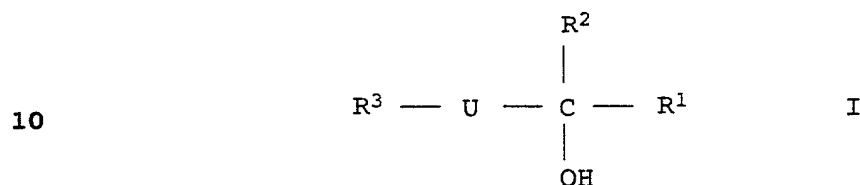
based on the electrolysis liquid.

13. (Amended) A process as claimed in [any one of claims 1 to 12] claim 1, where the electrolysis is carried out in an undivided electrolysis cell.

14. (Amended) A process as claimed in [any one of claims 1 to 13] claim 1, where the anodes employed are made of noble metals, noble-metal oxides, graphite or carbon materials, and the cathodes employed are made of iron, steel, nickel, zinc, noble metals, graphite or carbon materials.--

Preparation of α -oxidized carbonyl compounds

The present invention relates to a process for the preparation of
5 a compound of the general formula I

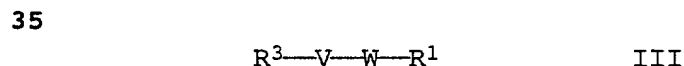


- where R^1 , R^2 , R^3 are hydrogen, C_1 - to C_{20} -alkyl, C_2 - to
15 C_{20} -alkenyl, C_2 - to C_{20} -alkynyl, C_3 - to C_{12} -cycloalkyl, C_4 - to
 C_{20} -cycloalkyl-alkyl, C_1 - to C_{20} -hydroxyalkyl, or aryl or C_7 - to
 C_{20} -arylalkyl which is unsubstituted or substituted by C_1 - to
 C_8 -alkyl, C_1 - to C_8 -alkoxy, halogen, C_1 - to C_4 -haloalkyl, C_1 - to
 C_4 -haloalkoxy, phenyl, phenoxy, halophenyl, halophenoxy, carboxyl,
20 C_2 - to C_8 -alkoxycarbonyl or cyano, or R^1 and R^2 or R^3 together are
a C_2 - to C_9 -alkanediyl unit which is unsubstituted,
monosubstituted or disubstituted by C_1 - to C_8 -alkyl, C_1 - to
 C_8 -alkoxy and/or halogen and in which one or two methyl groups may
also be replaced by a $(\text{CH}=\text{CH})$ unit and R^3 is additionally an
25 acetylated carbonyl group in which the alkoxy groups are derived
from an alcohol of the general formula II



- 30 where R^4 is C_1 - to C_6 -alkyl, and

U is an acetylated carbonyl group in which the alkoxy groups are
derived from an alcohol of the general formula II, or
is a compound of the general formula III



- where R^1 is as defined under the formula I, and R^3 is
exclusively aryl which is unsubstituted or substituted by C_1 -
40 to C_8 -alkyl, C_1 - to C_8 -alkoxy, halogen, C_1 - to C_4 -haloalkyl,
 C_1 - to C_4 -haloalkoxy, phenyl, phenoxy, halophenyl,
halophenoxy, carboxyl, C_2 - to C_8 -alkoxycarbonyl or cyano,

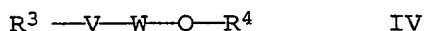
- V is a carbonyl group or is as defined for U under the formula
45 I, and

2

W is as defined for V, with the proviso that one of the groups V and W is a carbonyl group and the other is an acetylated carbonyl group,

5 or

a compound of the general formula IV

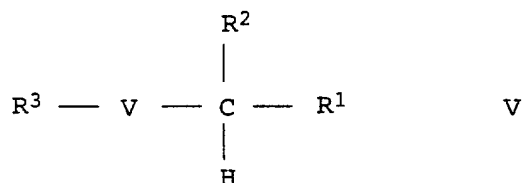


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where R^4 is as defined under the formula II, V and W are as defined under the formula II, and R^3 is as defined under the formula III,

15 by subjecting a compound of the general formula V

20



where V, R^1 , R^2 and R^3 are as defined under the formula I or III,
25 with the proviso that

- in the case where a compound of the formula III is desired, use is only made of a compound Va in which

30 R^1 is exclusively hydrogen and

R^3 is exclusively aryl which is unsubstituted or substituted by C_1 - to C_8 -alkyl, C_1 - to C_8 -alkoxy, halogen, C_1 - to C_4 -haloalkyl, C_1 - to C_4 -haloalkoxy, phenyl, phenoxy,
35 halophenyl, halophenoxy, carboxyl, C_2 - to C_8 -alkoxycarbonyl or cyano, and

- in the case where a compound of the formula IV is desired, use is only made of a compound Vb in which

40

R^1 and R^2 are exclusively hydrogen,

R^3 is exclusively aryl which is unsubstituted or substituted by C_1 - to C_8 -alkyl, C_1 - to C_8 -alkoxy, halogen, C_1 - to C_4 -haloalkyl, C_1 - to C_4 -haloalkoxy, phenyl, phenoxy,
45

halophenyl, halophenoxy, carboxyl, C₂- to
C₈-alkoxycarbonyl or cyano,

to an electrochemical reaction with an alcohol of the general
5 formula II in the presence of an auxiliary electrolyte and
catalytic amounts of a metal salt (S) derived from a metal from
the 1st, 2nd, 6th or 8th sub-group or from lead, tin or rhenium.

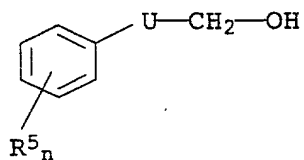
EP-A-460 451 discloses a process for the preparation of
10 α -hydroxymethyl ketals by electrochemical oxidation of aldehydes
or ketones in the presence of alcohols and halogen compounds as
auxiliary electrolytes. Repetition of the examples shows that
more highly oxidized carbonyl compounds are also formed under the
process conditions described if the carbonyl group is in the
15 α -position to an aromatic radical. Thus, for example, a methylene
group in the α -position to the carbonyl group can be oxidized to
the carbonyl function and in addition the aldehyde or keto
carbonyl group originally present can be oxidized to the carboxyl
group. Thus, it is not only α -hydroxyketals that are formed, but
20 also α -ketaldehydes, α -ketoacetals, α -ketalcarboxylic esters and
 α -keto orthoesters. However, this process is still not entirely
satisfactory since the overall yield of these target products is
relatively low and in addition large amounts of other
substantially unusable products are formed.
25 German Patent Application 19904929, which is not a prior
publication, relates to a process for the preparation of
2,2,3,3-tetramethoxypropanol by electrochemical oxidation of
methylglyoxal dimethyl acetal using a mixture comprising
30 methanol, water and an auxiliary electrolyte as electrolysis
medium and an iron, steel, platinum or zinc cathode.

It is an object of the present invention to provide an
electrochemical process by means of which α -hydroxyketals,
35 α -ketalaldehydes, α -ketoacetals, α -ketalcarboxylic esters and
 α -keto orthoesters can be prepared from keto or aldehyde carbonyl
compounds. We have found that this object is achieved by the
process defined above.

40 The process according to the invention is particularly suitable
for the preparation of compounds of the general formulae I, III
and IV, where the radical R⁴ in the acetylated carbonyl group is
derived from methanol or ethanol.

45 Of the compounds of the formula I, preference is given to those
of the formula Ia

4



Ia

5

where U is as defined in formula I,

n is 0, 1, 2 or 3, and

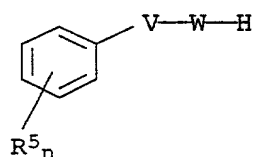
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R⁵ is C₁- to C₈-alkyl, C₁- to C₈-alkoxy, halogen, C₁- to C₄-haloalkyl, C₁- to C₄-haloalkoxy, phenyl, phenoxy, halophenyl, halophenoxy, carboxyl, C₂- to C₈-alkoxycarbonyl or cyano.

15

Preference is likewise given to compounds of the general formula IIIa

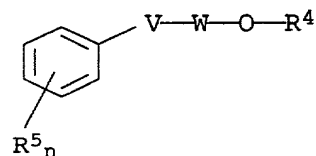
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IIIa

25 where n, V, W and R⁵ are as defined under the formula Ia or III, or of the general formula IVa

30

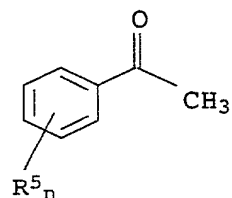


IVa

35 where n, V, W, R⁴ and R⁵ are as defined under the formula Ia or IIIa.

These compounds are prepared by employing as starting compound of the general formula V a compound of the general formula Va

40



Va

45

5

where n and R⁵ are as defined under the formula Ia.

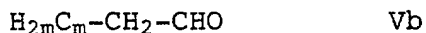
The process is furthermore particularly suitable for the preparation of compounds of the general formula Ib

5



where m is a number from 1 to 10, and R⁴ is as defined in formula II, and for whose preparation use is made of a compound of the

10 general formula Vb



The process is very particularly suitable for the preparation of

15

- 2-phenyl-2,2-dimethoxyethanol,
2-phenyl-2,2-dimethoxyacetaldehyde and 2-phenylglyoxal
dimethyl acetal from methanol and acetophenone

- 20 - α -hydroxyoctanal dimethyl acetal from octanal and

- 2,2,3,3-tetramethoxypropanol from methylglyoxal dimethyl
acetal.

- 25 The auxiliary electrolyte present in the electrolysis solution is generally a halogen-containing auxiliary electrolyte, such as elemental halogen, an alkyl halide or a hydrogen halide.

Halogen-containing salts, in particular iodides or bromides, can also preferably be employed. Examples are ammonium halides, such

- 30 as ammonium bromide, ammonium iodide and tetrabutylammonium iodide. Particularly preferred metal halides are furthermore alkali metal halides, such as sodium bromide, sodium iodide, potassium iodide and potassium bromide.

- 35 The metal salts (S) are preferably those derived from mineral acids. The anions of the metal salt are thus, for example, phosphate, sulfate, nitrate, perchlorate or halide.

The cations of the metal salt (S) are preferably iron, nickel,

- 40 platinum, palladium, cobalt, zinc, silver or copper ions. The metal salt (S) is generally added to the electrolysis solution in amounts such that its metal ions are present therein in amounts of from 1 to 1000 ppm by weight, preferably from 5 to 500 ppm by weight, particularly preferably from 5 to 300 ppm by weight,

- 45 based on the total amount of electrolysis liquid.

If desired, conventional co-solvents are added to the electrolysis liquid. These are the inert solvents having a high oxidation potential which are generally conventional in organic chemistry. Examples which may be mentioned are dimethyl carbonate
5 and propylene carbonate. Besides said co-solvents, water can also be added to the electrolysis liquid, although the water content should not exceed 5% by weight, based on the total amount of electrolysis liquid.

10 In general, the electrolysis liquid has the following composition:

- a starting compound of the general formula V
 - 15 - an alcohol of the general formula II
 - a halogen-containing auxiliary electrolyte
 - catalytic amounts of the metal salt (S)
 - 20 - possibly the desired products of the general formulae I, III and IV
 - possibly other by-products of electrolysis which are derived
25 from the compounds of the general formulae I, II, III, IV and V
 - if desired, other conventional co-solvents.
- 30 The ratio between the products of the general formulae I and V and the other by-products to the starting compounds in the electrolysis liquid and the ratio of the individual products having different degrees of oxidation to one another is of course, dependent on the progress of the reaction.
- 35 The ratio between the products of the general formulae I, III, IV and V and the other by-products to the starting compounds in the electrolysis liquid and the ratio of the individual products having different degrees of oxidation to one another is of course
40 dependent on the progress of the reaction.

In general, the amount of charge expended for the reaction is from 1 to 7 F per mole of starting compound of the general formula V. From 3.5 to 4 F are preferably employed if mixtures
45 are desired which are intended to contain, as principal components, compounds of the formulae I and III, and from 4.5 to 5.5 F are employed if mixtures are desired which are intended to

contain, as principal components, compounds of the formulae I and IV.

The process according to the invention can be carried out in all conventional types of electrolysis cell. Preference is given to undivided flow cells.

The current densities at which the process is carried out are generally from 0.5 to 25 A/dm². The temperatures are usually from -20 to 60°C, preferably from 0 to 60°C. The process is generally carried out at atmospheric pressure. Higher pressures are preferably used if higher temperatures are to be used in order to prevent the starting compounds or co-solvents from boiling.

Examples of suitable anode materials are noble metals such as platinum, or metal oxides, such as ruthenium or chromium oxide, or mixtures of the RuO_x/TiO_x type. Preference is given to graphite or carbon electrodes.

Suitable cathode materials are generally iron, steel, nickel, and noble metals, such as platinum and graphite and carbon materials.

When the reaction is complete, the electrolysis liquid is worked up by general separation methods. To this end, the electrolysis liquid is generally first distilled, and the individual compounds are obtained separately in the form of different fractions. Further purification can be carried out, for example, by crystallization or chromatography.

Experimental part

All experiments were carried out in an undivided cell having 11 bipolar electrodes (10 gaps, gap separation 1.5 mm).

Current density: 3.4 A/dm²

Flow rate: 400 l/h

Example 1:

40

Batch:

450 g of acetophenone
30 g of potassium iodide
2460 g of methanol
Fe(III): 5 ppm

45 Cathode:

steel 1.4301

Anode:

graphite

Duration:

7.03 h

Temperature: 36°C
 Amount of charge: 3.5 F
 Current strength: 5 A
 Conversion: >99%

5 Yields of the target products:

2-phenyl-2,2-dimethoxyethanol: 24%
 2-phenyl-2,2-dimethoxyacetaldehyde: 42%
 2-phenylglyoxal dimethyl acetal: 0%
 phenylglyoxylic acid methyl orthoester and methyl

10 2-phenyl-2,2-dimethoxy acetate: 0%
 Total: 66%

Example 2:

15 Batch: 450 g of acetophenone
 30 g of potassium iodide
 2460 g of methanol
 Fe(III): 5 ppm
 Cathode: Graphite
 20 Anode: Graphite
 Duration: 7.03 h
 Temperature: 36°C
 Amount of charge: 3.5 F
 Current strength: 5 A
 25 Conversion: 84%

Yields of the target products:

2-phenyl-2,2-dimethoxyethanol: 15%
 30 2-phenyl-2,2-dimethoxyacetaldehyde: 24%
 2-phenylglyoxal dimethyl acetal: 8%
 phenylglyoxylic acid methyl orthoester and methyl
 2-phenyl-2,2-dimethoxy acetate: 3%
 Total: 50%

35

Example 3 (4118/98-176):

Batch: 450 g of acetophenone
 90 g of potassium iodide
 2460 g of methanol
 Fe(III): 5 ppm
 Cathode: steel 1.4301
 Anode: graphite
 Duration: 7.03 h
 45 Temperature: 55-58°C
 Amount of charge: 3.5 F
 Current strength: 5 A

Conversion: 88%

Yields of the target products:

2-phenyl-2,2-dimethoxyethanol: 38%

2-phenyl-2,2-dimethoxyacetaldehyde: 19%

5 2-phenylglyoxal dimethyl acetal: 12%

phenylglyoxylic acid methyl orthoester and methyl

2-phenyl-2,2-dimethoxy acetate: 1%

Total: 70%

10 Example 4:

Batch: 450 g of acetophenone
90 g of potassium iodide
2460 g of methanol

15 Fe(III): 5 ppm

Cathode: steel 1.4301

Anode: graphite

Duration: 10.47 h

Temperature: 55-58°C

20 Amount of charge: 5.5 F

Current strength: 5 A

Conversion: >99%

Yields of the target products:

2-phenyl-2,2-dimethoxyethanol: 39%

25 2-phenyl-2,2-dimethoxyacetaldehyde: 0%

2-phenylglyoxal dimethyl acetal: 3%

phenylglyoxylic acid methyl orthoester and methyl

2-phenyl-2,2-dimethoxy acetate: 39%

30 Example 5:

Batch: 450 g of octanal
90 g of potassium iodide
2460 g of methanol

35 Fe(III): 5 ppm

Cathode: MKUS-F04 (SGL)

Anode: Graphite felt RVG 2003, 6 mm
(Deutsche Carbon)

Duration: 3.76 h

40 Temperature: 55-58°C

Amount of charge: 2 F

Current strength: 5 A

Conversion: >99%

Yield: 37% α -hydroxyoctanal dimethyl

45 acetal

Example 6:

Batch: 450 g of octanal
90 g of potassium iodide
2460 g of methanol
Fe(III): 5 ppm
Cathode: MKUS-F04 (SGL)
Anode: Graphite felt RVG 2003, 6 mm
(Deutsche Carbon)
10 Duration: 3.76 h
Temperature: 26-28°C
Amount of charge: 2 F
Current strength: 5 A
Conversion: 97%
15 Yield: 45% α -hydroxyoctanal
dimethyl acetal

Example 7:

20 Batch: 450 g of methylglyoxal
dimethyl acetal
45 g of potassium iodide
2505 g of methanol
0.11 g NiSO₄
25 Cathode: graphite
Anode: graphite
Duration: 5 h
Temperature: 30°C
Current strength: 5 A
30 Conversion: 52%
Selectivity: 59.4%
Yield of 2,2,3,3-tetramethoxypropanol: 31%

Comparative Example 1:

35 Batch: 450 g of acetophenone
30 g of potassium iodide
2460 g of methanol
Cathode: steel 1.4301
40 Anode: graphite
Duration: 7,03 h
Temperature: 36°C
Amount of charge: 3.5 F
Current strength: 5 A
45 Conversion: 98%
Yields of the target products:
2-phenyl-2,2-dimethoxyethanol: 19%

11

2-phenyl-2,2-dimethoxyacetaldehyde: 12%
2-phenylglyoxal dimethyl acetal: 5%
phenylglyoxylic acid methyl orthoester and methyl
2-phenyl-2,2-dimethoxy acetate: 9%
5 Total: 45%

Comparative Example 2:

10 Batch: 450 g of acetophenone
30 g of potassium iodide
2460 g of methanol
Cathode: graphite
Anode: graphite
Duration: 7.03 h
15 Temperature: 36°C
Amount of charge: 3.5 F
Current strength: 5 A
Conversion: 95%
Yields of the target products:
20 2-phenyl-2,2-dimethoxyethanol: 7%
2-phenyl-2,2-dimethoxyacetaldehyde: 25%
2-phenylglyoxal dimethyl acetal: 3%
phenylglyoxylic acid methyl orthoester and methyl
2-phenyl-2,2-dimethoxy acetate: 1%
25 Total: 36%

Comparative Example 3:

30 Batch: 450 g of octanal
90 g of potassium iodide
2460 g of methanol
Cathode: graphite
Anode: graphite
Duration: 3.76 h
35 Temperature: 55-58°C
Amount of charge: 2 F
Current strength: 5 A
Conversion: >99%
Yield: 30%

40

Comparative Example 4:

45 Batch: 450 g of octanal
90 g of potassium iodide
2460 g of methanol
Cathode: graphite
Anode: graphite

12

Duration: 3.76 h
Temperature: 26-28°C
Amount of charge: 2 F
Current strength: 5 A
5 Conversion: >99%
Yield: 40%

Comparative Example 5:

10 Batch: 450 g of methylglyoxal
dimethyl acetal
45 g of potassium iodide
2505 g of methanol
Cathode: graphite
15 Anode: graphite
Duration: 5 h
Temperature: 30°C
Current strength: 5 A
Conversion: >99%
20 Selectivity: 24.6%
Yield: 24.6% 2,2,3,3-tetramethoxypropanol

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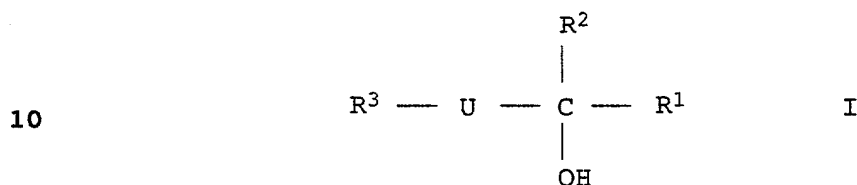
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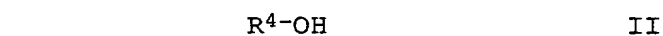
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We claim:

1. A process for the preparation of a compound of the general
5 formula I



where R^1 , R^2 , R^3 are hydrogen, C_1 - to C_{20} -alkyl, C_2 - to
15 C_{20} -alkenyl, C_2 - to C_{20} -alkynyl, C_3 - to C_{12} -cycloalkyl, C_4 - to
 C_{20} -cycloalkyl-alkyl, C_1 - to C_{20} -hydroxyalkyl, or aryl or C_7 -
to C_{20} -arylalkyl which is unsubstituted or substituted by C_1 -
to C_8 -alkyl, C_1 - to C_8 -alkoxy, halogen, C_1 - to C_4 -haloalkyl,
20 C_1 - to C_4 -haloalkoxy, phenyl, phenoxy, halophenyl,
halophenoxy, carboxyl, C_2 - to C_8 -alkoxycarbonyl or cyano, or
 R^1 and R^2 or R^3 together are a C_2 - to C_9 -alkandiyl unit which
is unsubstituted, monosubstituted or disubstituted by C_1 - to
 C_8 -alkyl, C_1 - to C_8 -alkoxy and/or halogen and in which one or
25 R^3 is additionally an acetylated carbonyl group in which the
alkoxy groups are derived from an alcohol of the general
formula II



30 where R^4 is C_1 - to C_6 -alkyl, and

U is an acetylated carbonyl group in which the alkoxy groups
are derived from an alcohol of the general formula II, or
35 is a compound of the general formula III



where R^1 is as defined under the formula I, and R^3 is
40 exclusively aryl which is unsubstituted or substituted by C_1 -
to C_8 -alkyl, C_1 - to C_8 -alkoxy, halogen, C_1 - to C_4 -haloalkyl,
 C_1 - to C_4 -haloalkoxy, phenyl, phenoxy, halophenyl,
halophenoxy, carboxyl, C_2 - to C_8 -alkoxycarbonyl or cyano,

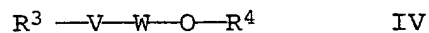
45 V is a carbonyl group or is as defined for U under the
formula I, and

14

W is as defined for V, with the proviso that one of the groups V and W is a carbonyl group and the other is an acetylated carbonyl group,

5 or

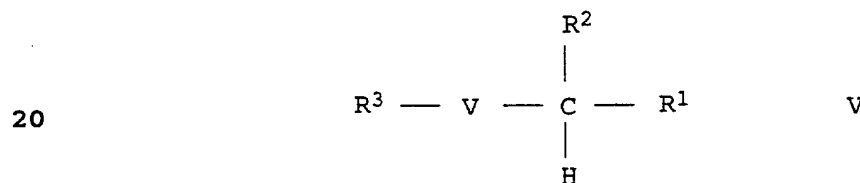
a compound of the general formula IV



10

where R^4 is as defined under the formula II, V and W are as defined under the formula II, and R^3 is as defined under the formula III,

15 by subjecting a compound of the general formula V



25 where V, R^1 , R^2 and R^3 are as defined under the formula I or III, with the proviso that

- in the case where a compound of the formula III is desired, use is only made of a compound Va in which

30 R^1 is exclusively hydrogen and

R^3 is exclusively aryl which is unsubstituted or substituted by C_1 - to C_8 -alkyl, C_1 - to C_8 -alkoxy, halogen, C_1 - to C_4 -haloalkyl, C_1 - to C_4 -haloalkoxy, phenyl, phenoxy, halophenyl, halophenoxy, carboxyl, C_2 - to C_8 -alkoxycarbonyl or cyano, and

35

- in the case where a compound of the formula IV is desired, use is only made of a compound Vb in which

40

R^1 and R^2 are exclusively hydrogen,

R^3 is exclusively aryl which is unsubstituted or substituted by C_1 - to C_8 -alkyl, C_1 - to C_8 -alkoxy, halogen, C_1 - to C_4 -haloalkyl, C_1 - to C_4 -haloalkoxy,

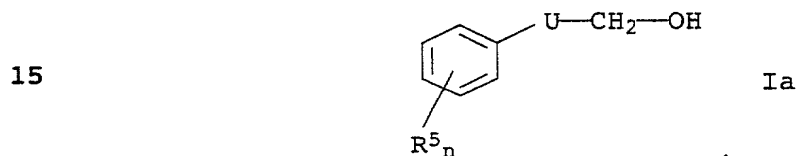
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phenyl, phenoxy, halophenyl, halophenoxy, carboxyl,
C₂- to C₈-alkoxycarbonyl or cyano,

5 to an electrochemical reaction with an alcohol of the general
formula II in the presence of an auxiliary electrolyte and
catalytic amounts of a metal salt (S) derived from a metal
from the 1st, 2nd, 6th or 8th sub-group or from lead, tin or
rhenium.

10 2. A process as claimed in claim 1 for the preparation of a
compound of the general formula Ia



where U is as defined under the formula I,

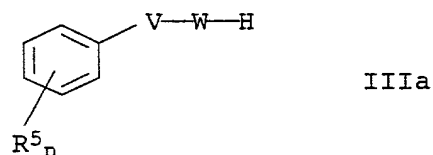
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n is 0, 1, 2 or 3, and

R⁵ is C₁- to C₈-alkyl, C₁- to C₈-alkoxy, halogen, C₁- to
C₄-haloalkyl, C₁- to C₄-haloalkoxy, phenyl, phenoxy,
25 halophenyl, halophenoxy, carboxyl, C₂- to
C₈-alkoxycarbonyl or cyano,

or of the general formula IIIa

30

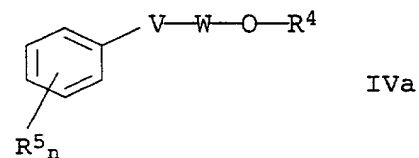


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where n, V, W and R⁵ are as defined under the formula Ia or
III,

or of the general formula IVa

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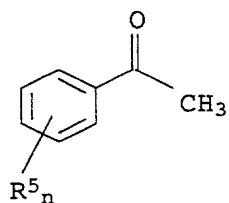


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where n, V, W, R⁴ and R⁵ are as defined under the formula Ia or IIIa, by employing, as starting compound of the general formula V, a compound of the general formula Va,

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Va

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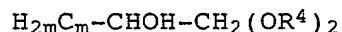
where n and R⁵ are as defined under the formula Ia.

3. A process as claimed in claim 2, where the compound of the general formula Ia is 2-phenyl-2,2-dimethoxyethanol, the compound of the general formula IIIa is 2-phenyl-2,2-dimethoxyacetaldehyde or 2-phenylglyoxal dimethyl acetal, the compound of the general formula IVa is phenylglyoxylic acid methyl orthoester, and the compound of the general formula Va is acetophenone.

20

4. A process as claimed in claim 1, where the compound of the general formula I is a compound of the general formula Ib

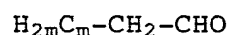
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Ib

where m is a number from 1 to 10, and R⁴ is as defined under the formula II, and the compound of the general formula V is a compound of the general formula Vb

30



Vb.

5. A process as claimed in any one of claims 1 to 4, where the compound of the formula I is 2,2,3,3-tetramethoxypropanol, and the starting compound employed is methylglyoxal dimethyl acetal.

35

6. A process as claimed in any one of claims 1 to 5, where the anions of the metal salt (S) are derived from mineral acids.

40

7. A process as claimed in any one of claims 1 to 6, where the anions of the metal salt (S) are phosphate, sulfate, nitrate, perchlorate or halide.

45

8. A process as claimed in any one of claims 1 to 7, where the cations of the metal salt (S) are iron, nickel, platinum, palladium, cobalt, zinc, silver or copper.
- 5 9. A process as claimed in any one of claims 1 to 8, where the electrolysis liquid contains from 1 to 1000 ppm by weight of metal ions of the metal salt (S), based on the total amount of electrolysis liquid.
- 10 10. A process as claimed in any one of claims 1 to 9, where the electrolysis liquid contains a halogen-containing auxiliary electrolyte.
11. A process as claimed in any one of claims 1 to 10, where the
15 electrolysis liquid essentially consists of
- a starting compound of the general formula V
 - an alcohol of the general formula II
 - 20 - a halogen-containing auxiliary electrolyte
 - catalytic amounts of the metal salt (S)
 - 25 - possibly the desired products of the general formulae I, III and IV
 - possibly other by-products of electrolysis which are derived from the compounds of the general formulae I, II, III, IV and V, and
 - 30 - if desired, other conventional co-solvents.
12. A process as claimed in any one of claims 1 to 11, where
35
- the proportion of the starting compounds and products of the general formulae I, III, IV and V and of the other by-products of electrolysis from the abovementioned compounds is from 1 to 70% by weight,
 - 40 - the proportion of the alcohol of the general formula II is from 14.9 to 94.9% by weight,
 - the proportion of auxiliary electrolyte is from 0.1 to 5% by weight, and
 - 45

18

- the proportion of any co-solvents present is from 0 to 70% by weight,

based on the electrolysis liquid.

5

13. A process as claimed in any one of claims 1 to 12, where the electrolysis is carried out in an undivided electrolysis cell.

- 10 14. A process as claimed in any one of claims 1 to 13, where the anodes employed are made of noble metals, noble-metal oxides, graphite or carbon materials, and the cathodes employed are made of iron, steel, nickel, zinc, noble metals, graphite or carbon materials.

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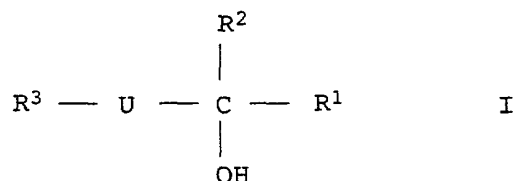
Preparation of α -oxidized carbonyl compounds

Abstract

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A process for the preparation of a compound of the general formula I

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where R^1 , R^2 , R^3 are hydrogen, C_1 - to C_{20} -alkyl, C_2 - to C_{20} -alkenyl, C_2 - to C_{20} -alkynyl, C_3 - to C_{12} -cycloalkyl, C_4 - to C_{20} -cycloalkyl-alkyl, C_1 - to C_{20} -hydroxyalkyl, or aryl or C_7 - to C_{20} -arylalkyl which is unsubstituted or substituted by C_1 - to C_8 -alkyl, C_1 - to C_8 -alkoxy, halogen, C_1 - to C_4 -haloalkyl, C_1 - to C_4 -haloalkoxy, phenyl, phenoxy, halophenyl, halophenoxy, carboxyl, C_2 - to C_8 -alkoxycarbonyl or cyano, or R^1 and R^2 or R^3 together are a C_2 - to C_9 -alkandiyl unit which is unsubstituted, monosubstituted or disubstituted by C_1 - to C_8 -alkyl, C_1 - to C_8 -alkoxy and/or

20 halogen and in which one or two methyl groups may also be replaced by a $(\text{CH}=\text{CH})$ unit and R^3 is additionally an acetylated carbonyl group in which the alkoxy groups are derived from an alcohol of the general formula II

30



where R^4 is C_1 - to C_6 -alkyl, and

U is an acetylated carbonyl group in which the alkoxy groups are

35 derived from an alcohol of the general formula II, or is a compound of the general formula III



40 where R^1 is as defined under the formula I, and R^3 is exclusively aryl which is unsubstituted or substituted by C_1 - to C_8 -alkyl, C_1 - to C_8 -alkoxy, halogen, C_1 - to C_4 -haloalkyl, C_1 - to C_4 -haloalkoxy, phenyl, phenoxy, halophenyl, halophenoxy, carboxyl, C_2 - to C_8 -alkoxycarbonyl or cyano,

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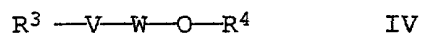
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V is a carbonyl group or is as defined for U under the formula I, and

W is as defined for V, with the proviso that one of the groups
 5 V and W is a carbonyl group and the other is an acetylated carbonyl group,

or

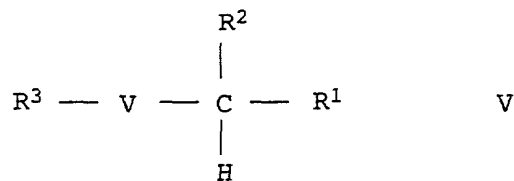
10 a compound of the general formula IV



where R^4 is as defined under the formula II, V and W are as
 15 defined under the formula II, and R^3 is as defined under the formula III,

by subjecting a compound of the general formula V

20



25

where V, R^1 , R^2 and R^3 are as defined under the formula I or III, with the proviso that

30 - in the case where a compound of the formula III is desired, use is only made of a compound Va in which

R^1 is exclusively hydrogen and

35 R^3 is exclusively aryl which is unsubstituted or substituted by C_1 - to C_8 -alkyl, C_1 - to C_8 -alkoxy, halogen, C_1 - to C_4 -haloalkyl, C_1 - to C_4 -haloalkoxy, phenyl, phenoxy, halophenyl, halophenoxy, carboxyl, C_2 - to C_8 -alkoxycarbonyl or cyano, and

40

- in the case where a compound of the formula IV is desired, use is only made of a compound Vb in which

R^1 and R^2 are exclusively hydrogen,

45

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R³ is exclusively aryl which is unsubstituted or substituted by C₁- to C₈-alkyl, C₁- to C₈-alkoxy, halogen, C₁- to C₄-haloalkyl, C₁- to C₄-haloalkoxy, phenyl, phenoxy, halophenyl, halophenoxy, carboxyl, C₂- to C₈-alkoxycarbonyl or cyano,

to an electrochemical reaction with an alcohol of the general formula II in the presence of an auxiliary electrolyte and catalytic amounts of a metal salt (S) derived from a metal from the 1st, 2nd, 6th or 8th sub-group or from lead, tin or rhenium.

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Declaration, Power of Attorney

Page 1 of 3

0050/050554

We (I), the undersigned inventor(s), hereby declare(s) that:

My residence, post office address and citizenship are as stated below next to my name,

We (I) believe that we are (I am) the original, first, and joint (sole) inventor(s) of the subject matter which is claimed and for which a patent is sought on the invention entitled

PREPARATION OF α -OXIDIZED CARBONYL COMPOUNDS

the specification of which

☐ is attached hereto.

☐ was filed on _____ as

Application Serial No. _____

and amended on _____.

☒ was filed as PCT international application

Number PCT/EP00/07026

on July 21, 2000

and was amended under PCT Article 19

on _____ (if applicable).

We (I) hereby state that we (I) have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

We (I) acknowledge the duty to disclose information known to be material to the patentability of this application as defined in Section 1.56 of Title 37 Code of Federal Regulations.

We (I) hereby claim foreign priority benefits under 35 U.S.C. § 119(a)-(d) or § 365(b) of any foreign application(s) for patent or inventor's certificate, or § 365(a) of any PCT International application which designated at least one country other than the United States, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate, or PCT International application having a filing date before that of the application on which priority is claimed. Prior Foreign Application(s)

Application No.	Country	Day/Month/Year	Priority Claimed
19937108.3	Germany	06 August 1999	<input checked="" type="checkbox"/> Yes <input type="checkbox"/> No

We (I) hereby claim the benefit under Title 35, United States Codes, § 119(e) of any United States provisional application(s) listed below.

(Application Number)

(Filing Date)

(Application Number)

(Filing Date)

We (I) hereby claim the benefit under 35 U.S.C. § 120 of any United States application(s), or § 365(c) of any PCT International application designating the United States, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT International application in the manner provided by the first paragraph of 35 U.S.C. § 112, I acknowledge the duty to disclose information which is material to patentability as defined in 37 CFR § 1.56 which became available between the filing date of the prior application and the national or PCT International filing date of this application.

Application Serial No.

Filing Date

Status (pending, patented,
abandoned)

_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____

And we (I) hereby appoint:

Norman F. Oblon, Registration Number 24, 618;
 Marvin J. Spivak, Registration Number 24, 913;
 Gregory J. Maier, Registration Number 25, 599;
 William E. Beaumont, Registration Number 30, 996;
 Steven B. Kelber, Registration Number 30, 073;
 Jean-Paul Lavalleye, Registration Number 31, 451;
 Timothy R. Schwartz, Registration Number 32, 171;
 Stephen G. Baxter, Registration Number 32, 884;
 Richard L. Treanor, Registration Number 36, 379;
 Robert W. Hahl, Registration Number 33, 893, our (my) attorneys, with full

powers of substitution and revocation, to prosecute this application and to transact all business in the Patent Office connected therewith; and we (I) hereby request that all correspondence regarding this application be sent to the firm of OBLON, SPIVAK, McCLELLAND, MAIER & NEUSTADT, P. C., whose Post Office Address is: Fourth Floor, 1755 Jefferson Davis Highway, Arlington, Virginia 22202.

We (I) declare that all statements made herein of our (my) own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

100 Hermann Pütter

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Signature of Inventor

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